

MANUFACTURE OF AMMONIUM SULFATE FERTILIZER FROM FGD-GYPSUM

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ABSTRACT

The goal of this study is to assess the technical and economic feasibility of producing marketable products, namely fertilizer-grade ammonium sulfate and calcium carbonate, from gypsum produced as part of lime/limestone flue gas desulfurization (FGD) processes. Millions of tons of FGD-gypsum by-product will be produced in this decade. In this study, a literature review and bench-scale experiments were conducted to obtain process data for the production of marketable products from FGD-gypsum and to help evaluate technical and economic feasibility of the process. FGD-gypsum produced at the Abbott power plant in Champaign, IL was used as a raw material. The scrubber, a Chiyoda Thoroughbred 121 FGD, produced a filter cake product contains 98.36% gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and less than 0.01% calcium sulfite (CaSO_3). Conversion of FGD-gypsum to ammonium sulfate were tested at temperatures between 60 to 70°C for a duration of five to six hours. The results of a literature review and preliminary bench-scale experiments are presented in this paper.

INTRODUCTION

The 1990 amendments to the Clean Air Act mandate a two-stage, 10-million ton reduction in sulfur dioxide emissions in the United States¹. Plants burning high sulfur coal and using FGD technologies must also bear increasingly expensive landfill disposal costs for the solid waste produced². The FGD technologies would be less of a financial burden if successful commercial uses were developed for the gypsum-rich by-products of the wet limestone scrubbing.

The degree to which FGD-gypsum is commercially used depends on its quality. Currently, high-quality FGD-gypsum with purity greater than 94% is used mainly to manufacture construction materials, i.e. stucco and gypsum-plaster, gypsum wall boards, and cement³. The amount of high quality FGD gypsum could exceed the current demand of the FGD-gypsum industry. Conversion of FGD-gypsum to marketable products could be a deciding factor in the continued use of high-sulfur Illinois coals by electric utilities. One approach is to produce cost-competitive ammonium sulfate fertilizer and commercial-grade calcium carbonate from FGD-gypsum.

Ammonium sulfate is a valuable source of both nitrogen and sulfur nutrients for growing plants. There is an increasing demand for sulfur in the sulfate form as a plant nutrient because of diminished deposition of atmospheric sulfur compounds from flue gas emissions and more sulfur is taken up by plants produced in high yields⁴. Also, the trend of using high-nitrogen content fertilizers has pressed incidental sulfur compounds out of traditional fertilizer. The current market for ammonium sulfate in the United States is about two million tons per year. It is anticipated that 5 to 10 million tons of new ammonium sulfate production may be required for fertilizer markets annually to make up for the loss of sulfur deposition from the increased restriction on acid-rain. The fertilizer industry appears ready to accept an added source of fertilizer grade ammonium sulfate to supply sulfur in NPK fertilizer blends⁵.

In Phase-I of this study, a literature review and a series of bench-scale experiments were conducted to obtain process data for the production of ammonium sulfate from FGD-gypsum and to help evaluate technical and economic feasibilities of the process.

EXPERIMENTAL PROCEDURES

Sample of FGD-gypsum and methods of analyses - The Abbott power plant in Champaign, Illinois operates a Chiyoda Thoroughbred 121 FGD-desulfurization system which produces one ton of gypsum for every ten tons of coal burned. The FGD-gypsum sample collected was dried in ambient air for two to four days. The particle size distributions of the sample were determined using both manual and instrumental methods. In the manual method, the sample was wet-sieved through a 100 mesh (149 μm) screen and then a 200 mesh (74 μm) screen. The weight % of the size-fractional samples were determined after drying. In the

instrumental method, a Micro Trac II analyzer was used to determine the mean and standard deviation of the particle diameter by means of laser light scattering.

The amounts of free water (released at 45°C) and combined water (released at 230°C for gypsum), calcium oxide (CaO), magnesium oxide (MgO), and carbon dioxide in the sample were determined by the ASTM method C471. Based on these analytical results, the compositions were calculated in terms of %CaCO₃, %MgCO₃, %CaSO₄, %CaSO₄·2H₂O, and %(NH₄)₂SO₄. Thermogravimetric analysis (TGA) was conducted under an air flow of 50 mL/min with programmed heating from room temperature to 900°C at 10°C/min. The weight loss profile was used for preliminary estimates of purity and composition of gypsum.

Conversion of FGD-gypsum to ammonium sulfate and calcium carbonate - The batch, bench-scale reactor system consisted of a 1000-mL, three-neck, round-bottomed flask fitted with a mechanical stirrer, a condenser, and a thermometer. An autotransformer and heating mantle were used to control the reaction temperature. The important reaction for producing ammonium sulfate from the FGD-gypsum is the reaction between ammonium carbonate and calcium sulfate. Two sets of experiments were conducted in this study. In the first set of experiments, the gypsum reacted with reagent-grade ammonium carbonate in a liquid medium. In the second set of experiments, ammonium carbonate, formed by the reaction of ammonia and carbon dioxide in a liquid medium reacted with suspended gypsum. The procedures for the experiments are outlined below.

FGD-gypsum was added to an ammonium carbonate solution (prepared by dissolving reagent-grade ammonium carbonate in 500 mL of distilled water) in the 1000-mL reaction flask. The temperature of the stirred mixture was raised from room temperature to the reaction temperature and maintained at that temperature for a range of pre-determined times. The solution which contained the ammonium sulfate product was separated from the solid byproduct, calcium carbonate, by vacuum filtration. The filtrate plus the rinsing, a total of about 600 mL of the liquid, was concentrated to a volume of about 150 mL in a constant temperature water bath. The residual concentrate was kept at room temperature to form ammonium sulfate crystals. The condensation and crystallization steps were repeated until no more crystal could be produced. The combined product was dried under ambient air before determining the total weight.

In the second set of experiments, ammonium carbonate was formed by the reaction of ammonia and carbon dioxide in a liquid medium, which was then allowed to react with FGD-gypsum in suspension. After removal of the calcium carbonate, the ammonium sulfate is recovered in a similar manner by filtration, evaporation and crystallization.

The ammonium sulfate produced was analyzed by melting point determination, chemical analysis and TGA analysis. The yield of the ammonium sulfate produced was obtained based on its theoretical yield from a total conversion of calcium sulfate feed. The purity of the ammonium sulfate produced was determined by chemical analysis of the nitrogen content using methods described by the Association of Agriculture Chemists (AOAC) and American Water Works Association (AWWA) procedure, and by ASTM method C-471. The calcium carbonate by-product was dried and subjected to TGA analyses to determine its purity and composition of unreacted gypsum.

RESULTS AND DISCUSSIONS

Characterization of the FGD-gypsum sample - The data on particle size distribution obtained by passing the gypsum sample through a series of screens and by Micro Trac II particle-size analyzer are shown in Table 1. About 84% of the sample has particle-size smaller than 74 µm (200 mesh), and about 99% of the sample has particles of smaller than 149 µm (100 mesh). The results of chemical analyses and the calculations following ASTM method C-471 are shown in Table 2. The FGD-gypsum sample has more combined water (water of hydration) than free moisture and has 98.36% gypsum (CaSO₄·2H₂O) with less than 0.01% of calcium sulfite (CaSO₃). The TGA curve of the gypsum sample is shown in Figure 1. All weight loss occurred between 98°C and 207°C (peak at 158.65°C). This weight loss is related to removal of the water of hydration from gypsum. No further thermal decomposition occurred to a temperature of 900°C.

Literature review - The chemistry of the process and process conditions⁶ were reviewed. The literature study showed that the production of ammonium sulfate from natural gypsum, ammonium, and carbon dioxide, known as the Merseburg Process, has been tried in England⁷ and India⁸ in 1951 and 1967, respectively. The process was proven to be

commercially feasible. The Merseburg Process for manufacturing ammonium sulfate from gypsum is based on the chemical reaction between gypsum and ammonium carbonate. Ammonium carbonate is formed by the reaction of ammonia and carbon dioxide in aqueous solution. The reaction produces insoluble calcium carbonate and an ammonium sulfate solution. The reason it is not currently used is the cost of natural gypsum and the availability of an economical source of carbon dioxide.

In the early 1960's, the chemistry of the Merseburg Process was carefully studied and partially developed in the U.S.. At that time the Tennessee Valley Authority (TVA) studied a process in which ammonium phosphate was produced using ammonium sulfate and phosphate rock as starting materials. In the process, phosphate rock was extracted with nitric acid. The extract was allowed to react with ammonium sulfate to produce ammonium phosphate. Gypsum was produced as a by-product. To minimize the costs of ammonium phosphate conversion, TVA adopted the Merseburg Process and developed a single-stage reactor both in bench scale⁹ and in pilot scale¹⁰ operations. The purpose was to recover the by-product gypsum and use it to regenerate ammonium sulfate for the starting material. In the regeneration, the by-product gypsum and ammonium carbonate were premixed before entering the reactor. Residence times of 0.5, 1, and 3 hours at 125°F (52°C) and 140°F (60°C) were tested, and conversions of greater than 95% were achieved⁹. Typical operating conditions in the pilot plant were 120°F (49°C), 2 hours residence time, and ammonium carbonate feed at or above 105% stoichiometric requirement, and the conversion was 98%¹⁰.

Bench scale testing for ammonium sulfate production - The important reaction for producing ammonium sulfate from the FGD-gypsum is the reaction between ammonium carbonate and calcium sulfate. Two sets of experiments (see experimental procedures section) were conducted in this study. The reaction conditions, amounts of reactants, and the properties of products for the two sets of experiments are listed in Table 3. The ammonium sulfate produced was confirmed both by comparing its melting point with that of a commercial standard and by examining chemical analysis data and TGA data. Based on the weight of the ammonium sulfate produced and its theoretical yield from a total conversion of calcium sulfate feed, a yield of up to 83% and a purity of up to 99% for the ammonium sulfate production was achieved. A mass balance calculation for calcium and sulfur in gypsum was conducted on experiment run No. 5 (Table 3). The results show a recovery of 98% for calcium in calcium carbonate and a recovery of 81% for sulfur in ammonium sulfate were obtained. The TGA curve for calcium carbonate produced in one of the residues is shown in Figure 2. The graph shows a weight loss occurring between 600°C and 770°C. This is attributed to the evolution of carbon dioxide from decomposing calcium carbonate. A typical TGA curve (Figure 3) of the ammonium sulfate produced shows a total decomposition of the sample with a maximum weight loss at 418.3°C.

In summary, the results of these preliminary laboratory experiments suggest that high quality ammonium sulfate can be produced from the FGD-gypsum sample obtained from the Abbott power plant.

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REFERENCES

1. E. Claussen, "Acid Rain: The Strategy," Office of Communications and Public Affairs, EPA Journal, Washington DC, Jan./Feb. 1991, vol. 17, no. 1.
2. R.E. Bolli and R.C. Forsythe, "Ohio Edison Company's Clean Coal Technology and Waste Utilization Programs," EPRI 1990 SO₂ Control Symposium, vol. 1, 3b.
3. S.K. Conn, M.G. Vacek, and J.T. Morris Jr., "Conversion from disposal to commercial grade gypsum; An alternative approach for disposal of scrubber wastes." EPRI 1993 SO₂ Control Symposium, vol. 3, 8b.
4. R.G. Hoeft, J.E. Sawyer, R.M. VandenHeuvel, MA. Schmitt, and G.S. Brinkman,

- Corn response to sulfur on Illinois soils, *J. Fert.*, 2:95-104, 1985.
- N.W. Frank and S. Hirano, "Utilization of FGD Solid Waste in the Form of By-product Agricultural Fertilizer," EPRI 1990 SO₂ Control Symposium, vol. 1, 3b.
 - Kirk-Othmer, *Encyclopedia of Chemical Technology*, fourth edition, vol. 2, 706, John Wiley & Sons, New York, 1992.
 - Higson, G.I., The Manufacture of Ammonium Sulphate from Anhydrite, *Chemistry and Industry*, 750-754, September 8, 1951.
 - Nitrogen, Conversion of Gypsum or Anhydrite to Ammonium Sulfate, *Nitrogen*, 46, March/April 1967.
 - Blouin, G.M., O.W. Livingston, and J.G. Getsinger, Bench-Scale Studies of Sulfate Recycle Nitric Phosphate Process, *J. Agr. Food Chem.*, vol. 18, 313-318, 1970.
 - Meline, R.S., H.L. Faucett, C.H. Davis, and A.R. Shirley Jr., Pilot-Plant Development of the Sulfate Recycle Nitric Phosphate Process, *Ind. Eng. Process Des. Develop.*, vol. 10, 257-264, 1971.

Table 1. Results of particle size analysis of the FGD-gypsum

Size	%
> 149 μm^1	0.97
149-74 μm^1	15.40
< 74 μm^1	83.60
average diameter (μm) ²	73.88
standard deviation ²	35.63

¹By sieve analysis; ²By Micro Trac II

Table 2. Results of ASTM chemical analysis of the FGD-gypsum

Analytes	Composition in wt. % moisture free basis
combined water	20.59
CaO	32.92
MgO	0.01
SO ₄	54.90
SO ₃	<0.01
CO ₂	0.71
NH ₃	<0.01
Free Moisture	<0.01
Calculated Values	
CaSO ₄ ·2H ₂ O	98.36
CaCO ₃	1.60
CaSO ₄	<0.01
CaSO ₃	<0.01
MgCO ₃	0.01
(NH ₄) ₂ SO ₄	<0.01

Table 3. Reaction conditions and the results of final product and by-product analyses

Run number	Run Conditions	¹ Mole ratio	CaCO ₃		(NH ₄) ₂ SO ₄		
			² Wt% in residue	³ Calculated yield	⁴ purity	³ Calculated yield	⁵ m.p. (°C)
1	70°C 5hr	1.56	97	ND	ND	ND	242
2	70°C 6hr	1.59	86	ND	95	82	237
3	70°C 6hr	1.33	81	81	ND	83	241
Run number	Run conditions	NH ₃ CO ₂		CaCO ₃		(NH ₄) ₂ SO ₄	
		mole/hr		² wt% in residue	³ calculated yield	⁴ purity	³ Calculated yield
4	60°C 4hr ⁶	1.50	1.25	ND	ND	99	58
5	65°C 6hr ⁶	1.25	1.00	94	104	95	83
6	70°C 6hr ⁶	1.25	1.00	ND	ND	90	76

¹The mole ratio of (NH₄)₂CO₃ to CaSO₄·2H₂O; ²Wt % CaCO₃ in residue by TGA;

³Based on theoretical yield from FGD-gypsum feed;

⁴Wet chemical analysis by ASTM C-471 and AWWA procedures;

⁵Melting point for the standard is 240°C; ⁶1.95 mole of gypsum used.

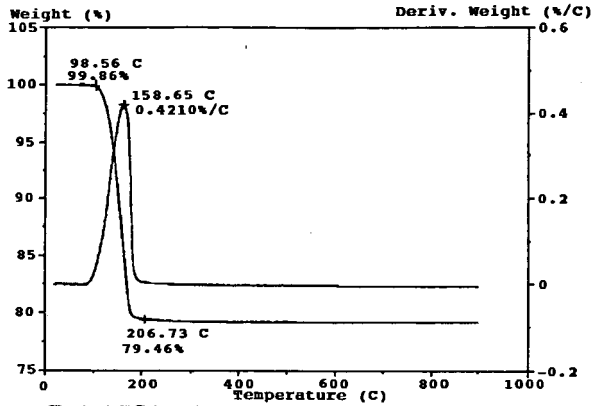


Figure 1: Typical TGA weight loss profile and first derivative for FGD-gypsum from the Abbott Plant.

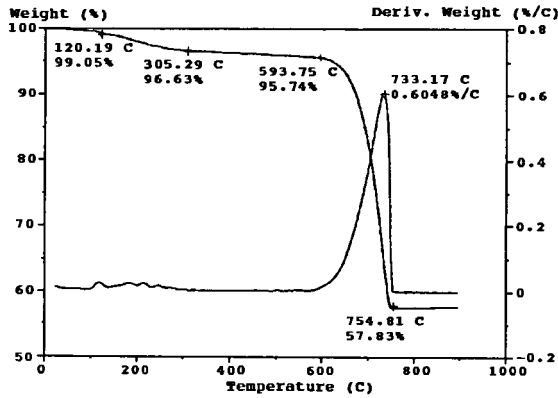


Figure 2: Typical TGA weight loss profile and first derivative for solid by-product (CaCO_3) from the ammonium sulfate production.

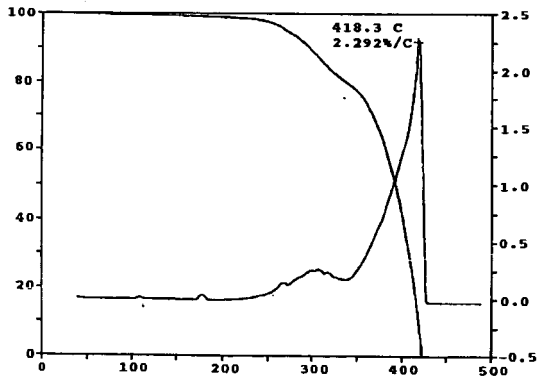


Figure 3: Typical TGA weight loss profile and first derivative of ammonium sulfate produced.